Name: Key

Chemistry 129 Spring 2017

General Chemistry

Examination #3:

Equations are provided.

You may use a calculator.

Show all your work!

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Bonus: ______/2

Total: ______/100

1. (12%) (a) Find K for the following reaction:

$$2NO_{2(g)} \leftrightarrow N_{2(g)} + 2O_{2(g)} \qquad (1) \qquad K_c = ?$$

Use the following data to find the unknown K_c.

$$\tfrac{1}{2} N_{2(g)} + \tfrac{1}{2} O_{2(g)} \leftrightarrow NO_{(g)} \qquad (2) \qquad K = 4.8 \times 10^{-10}$$

$$NO_{(g)} + \tfrac{1}{2} O_{2(g)} \leftrightarrow NO_{2(g)} \qquad (3) \qquad K = 301$$

$$\cancel{2NO_{(g)}} \rightleftharpoons N_{2(g)} + O_{2(g)} \qquad K = \left(\frac{1}{4.8\times10^{-10}}\right)^2$$

$$+\ 2NO_{2(g)} \rightleftharpoons \cancel{2NO_{(g)}} + O_{2(g)} \qquad K = \left(\frac{1}{301}\right)^2$$

$$2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$$

$$K_{overall} = \left(\frac{1}{4.8\times10^{-10}}\right)^2 \times \left(\frac{1}{301}\right)^2 = \underline{4.8\times10^{13}}$$

(b) When this reaction (1) comes to equilibrium, will the reaction mixture contain mostly reactant or mostly product? Why?

$K >> 1$ Mostly products at equilibrium (forward reaction is favored)

2. (12%) Classify the following salts as basic, acidic or neutral.

(i) NH_4I Acidic

(ii) $CsNO_2$ Basic

(iii) $Ba(ClO_3)_2$ Neutral

(iv) NaF Basic

(v) $Cr(NO_3)_3$ Acidic

(vi) KBr Neutral

3. (20%) Consider the ionization of pyridine:

$$C_5H_5N_{(aq)} + H_2O_{(l)} \leftrightarrow C_5H_5NH^+_{(aq)} + OH^-_{(aq)}$$

A 0.100M pyridine solution has a pH of 9.12. Determine the value of pyridine's base-ionization constant (K_b) and the equilibrium concentrations of C_5H_5N, $C_5H_5NH^+$, and OH^-.

$pOH = 14.00 - 9.12 = 4.88$

$[OH^-] = 10^{-4.88} = 1.3 \times 10^{-5} M$

$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

	$[C_5H_5N]$	$[C_5H_5NH^+]$	$[OH^-]$
I	0.100	0	0
C	-1.3×10^{-5}	$+1.3 \times 10^{-5}$	$+1.3 \times 10^{-5}$
E	$0.100 - 1.3 \times 10^{-5}$	1.3×10^{-5}	1.3×10^{-5}

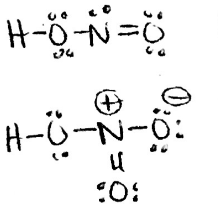
$$K_b = \frac{(1.3 \times 10^{-5})(1.3 \times 10^{-5})}{(0.100 - 1.3 \times 10^{-5})}$$

$K_b = \underline{1.7 \times 10^{-9}}$

$[C_5H_5N] = 0.100 M - 1.3 \times 10^{-5} M \cong \underline{0.100 M}$

$[C_5H_5NH^+] = [OH^-] = \underline{1.3 \times 10^{-5} M}$

4. (10%) (a) Which of the following acids has the larger pKa: **HNO_3** or **HNO_2**. Explain.



HNO_2 has a larger pKa because it is the weaker acid of the two (HNO_3 is a strong acid). HNO_3 has an additional oxygen atom (highly electronegative) which helps draw electron density away from N which in turn draws electron density away from the O—H bond. More polar bond, H comes off more easily.

(b) What is the chemical formula of the conjugate base of each of the acids in (a). Which is the stronger base? Explain.

Conjugate base of HNO_2: NO_2^-

Conjugate base of HNO_3: NO_3^-

NO_2^- is the conjugate base of the weaker acid so it is the stronger of the two bases.

5. (14%) The following reaction is exothermic.

$$Cu_2S_{(s)} + O_{2(g)} \leftrightarrow 2Cu_{(s)} + SO_{2(g)} \; + q$$

(a) Predict the effect (shift right, shift left, or no effect) of the following:

i. Adding more O_2 to the reaction mixture - shifts right
ii. Increasing the temperature of the reaction mixture - shifts left
iii. Adding more Cu to the reaction mixture - no effect
iv. Removing some SO_2 from the reaction mixture - shifts right
v. Compressing the vessel volume in half - no effect
vi. Adding a catalyst to the reaction mixture - no effect

(b) Will the equilibrium constant of the reaction increase or decrease if the temperature is decreased? Why?

$\downarrow T \Rightarrow$ Rx shifts right

K will be larger

6. (7%) Two unknown acid samples are studied by titration with a 0.100 M NaOH solution. One sample is **aspirin** (acetylsalicylic acid, pK_a = 3.52), and the other is **vinegar** (acetic acid, pK_a = 4.74). Which titration curve corresponds to which acid? Briefly explain.

for both acids

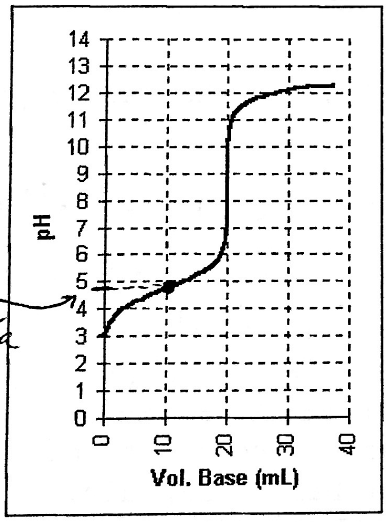
Equivalence Volume
↳ 20 mL

Midpoint ⇒ $\frac{V_e}{2} = 10 mL$

@ midpoint
pH = pKa

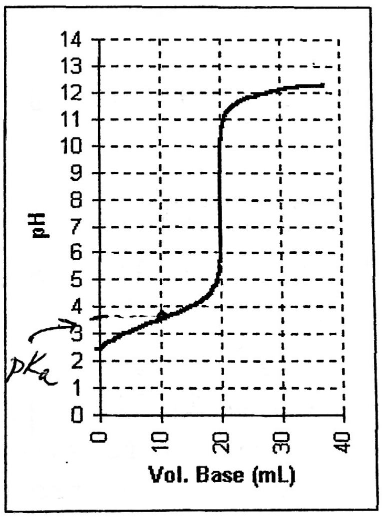
A

pKa



B

pKa



pKa ≅ 4.8

pKa ≅ 3.5

A: Vinegar
(Acetic Acid)

B: Aspirin
(Acetylsalicylic Acid)

7. (25%) Consider the titration of 30.00mL of 0.250M benzoic acid ($C_6H_5CO_2H$), pK_a = 4.20, with 0.300M KOH. Determine the equivalence volume and the pH at the following volumes of KOH added: **0 mL, 18.0mL, equivalence volume and 30.0mL.** Make sketch of the titration curve.

$$V_e = \frac{C_a V_a}{C_b} = \frac{(0.250M)(30.00mL)}{0.300M} = 25.0\,mL \qquad K_a = 10^{-4.20} = 6.3\times10^{-5}$$

V_b = 0 mL (Weak acid Soln)

$$[H_3O^+] = \sqrt{K_a \times [C_6H_5COOH]} = \sqrt{(6.3\times10^{-5})(0.250)} = 4.0\times10^{-3}M$$

$$pH = -\log(4.0\times10^{-3}) = \underline{\underline{2.40}}$$

V_b = 18.0 mL (Buffer Region)

	C_6H_5COOH	+ KOH ⟶	$C_6H_5CO_2K$	+ H_2O
BA	7.50 mmol			
A		5.40 mmol		
AA	2.10 mmol	0	5.40 mmol	

$$pH = -\log(6.3\times10^{-5}) + \log\frac{(5.40)}{(2.10)} = \underline{\underline{4.61}}$$

V_b = 25.0 mL (Equivalence Point - Weak base Soln)

	C_6H_5COOH	+ KOH ⟶	$C_6H_5CO_2K$	+ H_2O
BA	7.50 mmol			
A		7.50 mmol		
AA	0	0	7.50 mmol	

$$K_b = \frac{1.0\times10^{-14}}{6.3\times10^{-5}} = 1.6\times10^{-10}$$

$$[C_6H_5COO^-] = \frac{7.50\,mmol}{55.0\,mL} = 0.136M$$

$$[OH^-] = \sqrt{K_b \times [C_6H_5CO_2^-]} = \sqrt{(1.6\times10^{-10})(0.136)} = 4.7\times10^{-6}M$$

$$pOH = -\log(4.7\times10^{-6}) = 5.33 \qquad pH = 14.00 - 5.33 = \underline{\underline{8.67}}$$

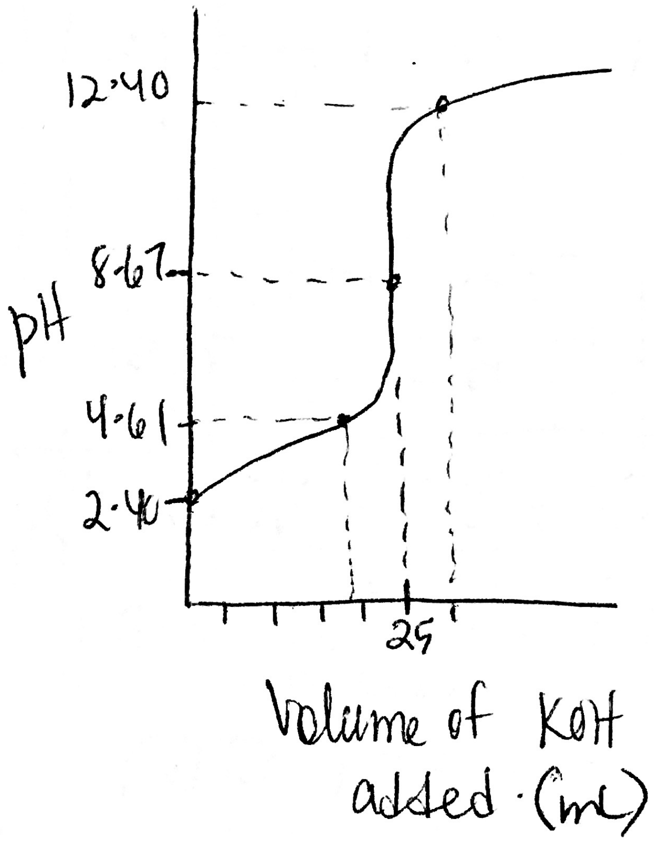
V_b = 30.0 mL (Excess KOH Soln)

	C_6H_5COOH	+ KOH ⟶	C_6H_5COOK	+ H_2O
BA	7.50 mmol			
A		9.00 mmol		
AA	0	1.50 mmol	7.50 mmol	

$$[OH^-] = [KOH] = \frac{1.50\,mmol}{60.0\,mL} = 0.0250$$

$$pOH = -\log(0.0250) = 1.60$$

$$pH = 14.00 - 1.60 = \underline{\underline{12.40}}$$


pH
12.40
8.67
4.61
2.40
25
Volume of KOH added (mL)

Bonus (2 pts):

Consider the following reaction:

$q + 2H_2O_{(g)} \leftrightarrow 2H_2{}_{(g)} + O_2{}_{(g)}$

If the reaction shifts right when the temperature is increased, is the reaction endothermic or exothermic?

Increasing T $\Rightarrow$ adding heat $\Rightarrow$ reaction is endothermic